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Paper Title: Integration of Nanofluids into Commercial Antifreeze Concentrates with ASTM D15 Corrosion Testing

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ABSTRACT: Originally five candidates of nano material were chosen for making stable nano dispersions. Nano graphite particles remain a practical choice for nanofluids thermal application after taking divergent performance attributes into full account: significant thermal conductivity increases, minimal viscosity increase, low density for better dispersion stability, and relatively low cost, among others. Three different types of commercial antifreeze coolants were chosen for the integration with graphite nano fluids. Without corrosion inhibitors our nano coolants typically fail both ASTM D15 engine coolant corrosion tests: D1384 and D4340. Yet, heating up and adding in electrolytes are two common ways to destroy a nano particle dispersion. After making adjustments in particle loading, choosing an effective dispersant, and establishing proper dispersant levels, two nano graphite coolants made from two different nano sources passed both engine coolant corrosion tests plus the CID AA-52624A compatibility and storage stability tests. Compared with the base fluid, the nano graphite coolant's thermal conductivity has more than a 25% increase at 2 volume percent particle loading, which is a significant enhancement.

KEYWORDS: graphite, alumina, nanofluids, thermal conductivity, ASTM D 15 corrosion tests.

Introduction

Inclusion of high thermal conductivity particles into fluid to enhance the thermal properties of the finished fluids had been tried as early as the 18th century [1]. However, before ultra-fine particles were available it had never been successful due to rapid particle settling and potential clogging in application. After nanotechnology emerged, the idea of dispersing nano particles into fluids to form nanofluids with unique properties has inspired broad interests of research in multiple domains in the first decade of 21st century. The most attractive performance enhancement of nanofluids has been the anomalous thermal conductivity increase observed [2-6]. Carbon nanotube dispersions once made a sensation with up to 300% thermal conductivity increases. However, at the same time, the viscosity increased by thousands of percent [7]. As a result, researchers mostly looked at nano metal and metal oxide particles. Using 'nanofluids' as the 'topic' to perform a SciFinder literature search, more than 3650 papers have been published so far (see Fig. 1). The publication surge of recent years is largely due to worldwide interest in the topic since thermal management is always of great importance in many industries. Refining the search with 'thermal', around 2500 papers are available. About two thirds of them deal with thermal conductivity or heat transfer. However there has not been any paper reporting the ASTM automotive coolant corrosion tests on nanofluids. The purpose of this paper is to achieve a stable

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nano dispersion that has significantly better thermal conductivity and passes the ASTM D 15 corrosion tests, and the CID AA-52624A compatibility and storage stability tests.

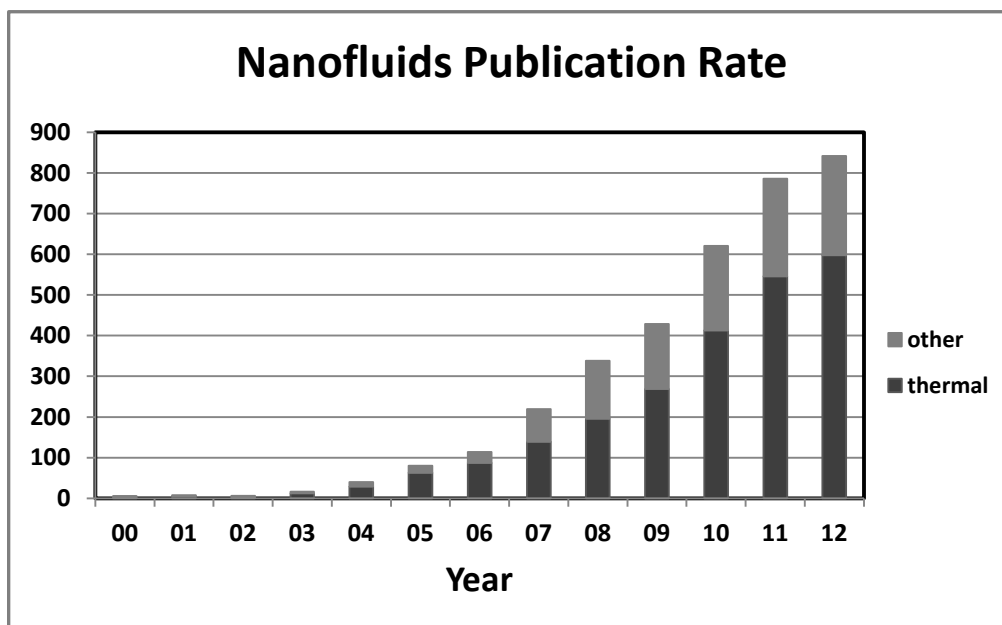


FIG. 1— *Nanofluids publication rate since year 2000.*

For a nanocoolant to have the best heat transfer effect, theoretically it must have higher thermal conductivity, higher heat capacity, higher density and lower viscosity. In reality, water has the highest heat capacity among common solids and liquids, so it is not practical for nanofluids to have a higher heat capacity in aqueous system. Since most solids have higher density than water and glycol, it is possible for nanofluids to have higher density than water glycol solution. However, density is dependent on particle loading and high density particles would incline to settle down much faster than lighter ones. In order to make a stable dispersion, lighter particles are more desirable. Besides, under the same mass percentage, lighter particles give a higher volume fraction which contributes more to thermal conductivity increase. With nano particles dispersed in a liquid, the viscosity always gets inevitably higher due to the surface interaction of particles and liquid molecules. The more and the finer the particles are, the higher the viscosity. Thus it is not practical for nanofluids to have lower viscosity either. Accordingly, this nanofluid research has focused on increasing thermal conductivity while minimizing viscosity increase.

The general trend is that nanoparticles with inherently higher thermal conductivity will produce nanofluids with higher thermal conductivity. Metals and carbon material such as diamond and nanotubes have the highest thermal conductivity. However they are also much more expensive and most metals have high density. Besides, nano metal particles have oxidation stability issues and nanotubes have health concerns [8]. There is also difficulty in making stable dispersions of nano metal particles and carbon nanotubes. Metals and carbon nanotubes with graphitic surfaces have free electrons and so are highly polarizable, which leads to the largest forces of attraction between the particles [9]. Thus aggregation will be hard to control and viscosity increase is inevitable. So metals and carbon nanotubes are excluded from our scope.

Originally five candidates were chosen: aluminum oxide (alumina), copper oxide, graphite, silicon carbide and diamond. These choices were made upon aforementioned reasoning and other considerations like commercial availability and literature popularity. They are summarized in Table 1.

TABLE 1—*A summary of properties and situations of five candidate materials.*

Materials	Thermal Conductivity k (W/mK)	Density d (g/cm ³)	Dispersability	Commercial Availability	Literature Popularity
Diamond	2300	3.5	low	low	low
Graphite	1000(x-plane) 5.5(y-plane)	2.25	medium	medium	low
Silicon Carbide	110	3.22	medium	medium	medium
Alumina	30	3.97	high	high	high
Copper oxide	18	6.31	high	high	high

Our first approach was focused on solving the practical nanofluids application barricade: stability. We employed a centrifugation method to accelerate the evaluation of the dispersion stability. After making stable nano dispersions, properties of thermal conductivity and viscosity were measured and evaluated to determine the next step candidates for corrosion tests. Eventually, graphite particles were identified as a practical choice after taking divergent performance attributes into account: significant thermal conductivity increases, minimal viscosity increase, low density for better dispersion stability, and relatively low cost, among others.

It is still challenging for nano fluids to perform well in ASTM D15 engine coolant corrosion tests D 1384 and D 4340. First, both tests are under high temperatures (around 200°F). Second, commercial antifreeze concentrates contain up to 5% electrolytes [10]. Yet, heating up and adding in electrolytes are two common ways to destroy a nano particle dispersion. Without corrosion inhibitors, our nano coolants typically fail both tests. Three different types of commercial antifreeze coolants were chosen for the integration of nano fluids. After making adjustments in particle loading, choosing an effective dispersant, and establishing proper dispersant levels, one nano graphite coolant was made from a commercially available graphite source that can pass ASTM engine coolant corrosion tests plus the CID AA-52624A compatibility and storage stability tests. Compared with the base fluid, this nano graphite coolant's thermal conductivity has more than a 25% increase at 2 volume percent particle loading, which is a significant enhancement.

Experimental

Thermal Conductivity Measurement

A KD2 Pro Thermal Property Analyzer by Decagon Devices was used to measure the thermal conductivity (k). It employed the transient hot wire technique and has an accuracy of $\pm 5\%$ when

the thermal conductivity is from 0.2 to 2 W/mK. A vial of glycerin provided by the manufacturer was used to do daily checks to make sure the data is within $\pm 5\%$.

Viscosity Measurement

Since nanofluids are mostly murky and sometimes stain, no automated viscometer was used. Instead a manual reverse-flow type kinematic viscometer by Cannon Instrument Company was used with the ASTM D 445 standard. The viscosity tubes were cleaned by ultrasonic cleaner after every use to remove any particle residue from the inside the tube wall.

Other Measurements

pH value was measured by a pH ISE Meter from Denver Instrument. The freezing point was measured by Phase Technology's 70 XAF Cloud, Pour and Freeze Point Lab Analyzer, or a portable Digital Refractometer from MISCO.

Centrifuge and Boil-up Tests

These two tests were in-house empirical tests. The centrifuge test was used to quickly evaluate the dispersion stability. After 50 minutes under 2000 RPM centrifuging, an unstable dispersion would have a clear top fluid, which indicates failure. Otherwise, the bottom sediments were collected, washed, dried and weighed. The sediment rate depends on particle sizes. Empirically if less than 20% of the particles settle under aforementioned centrifuge conditions, the dispersion is deemed stable and has potential of practical application. The boil-up test was used to see whether dispersions can survive heating. The nanofluid was boiled with boileezers under reflux for 5 hours, if agglomeration or gel up was observed, the test was regarded as a failure. Please note that both ASTM D 15 corrosion test are under high temperatures.

CID A-A-52624A Compatibility and Storage Stability Tests

These two tests were published by U.S. Army Tank-Automotive and Armaments Command.

ASTM D 15 Corrosion Tests

ASTM D 1384 Corrosion Test for Engine Coolants in Glassware and ASTM D 4340 Corrosion Test of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions were performed in Ashland Engine Lab, Ashland, KY.

Nano Materials

Alumina: 10nm, 20-30 nm, 40-80 nm powers were purchased from NanoAmor and 45 nm 50 mass% in water dispersion concentrate form Alfa Aesar (Nano Dur, 1121W , made by Nanophase). Sasol provided free powder samples Dispa X-0 (110 nm), X-30 (275 nm), 25F4 (108 nm), T25N4 (242 nm).

Copper oxide: was purchased from NanoAmor as powders (30-50 nm) and Alfa Aesar (made by Nanophase) as dispersion concentrate (NanoArc U1121W, 30 nm, 50 mass% in water).

Silicon carbide: Saint-Gobain provided free nano slurry samples (300 nm, 360 nm, 13 mass% in water). 80 nm powders were purchased from NanoAmor.

Diamond: 6 nm nano diamond powder samples were purchased from NanoAmor.

Graphite: nano graphite powders were purchased from NanoAmor (400nm) and GrafTech (GS-4E, 2000 nm), dispersion concentrate (in paste form) was purchased from Ladd Research (made by Acheson Colloid under brand name of Aquadag E with average particle size of 750 nm).

Dispersants

Solsperse 20000 and Solsperse 27000 were provided free from Lubrizol Company. Both are poly ether type and further detailed properties are proprietary. Dispersant T was provided free from Evonic Company, it is a poly glycol type dispersant and its specifics are also proprietary.

Blending and Milling

A Fisher Scientific Model 550 Sonic Disembrator was used in making nano dispersions. A horizontal 2L Laboratory Mill from Engineered Mills, Inc (Eiger) was also used to make even dispersion when needed.

Results and Discussion

Making Stable Nanofluids in Ethylene Glycol/Water Solution

The first stage evaluation was focused on dispersion stability and thermal conductivity increase (which was expected to be 20% or higher). Only when a nano dispersion is stable and has significant increase in thermal conductivity, it can be regarded as practical for use. The first stage evaluation was not tried with commercial antifreeze concentrate (Zerex Antifreeze). Instead pure ethylene glycol (EG) was used. Commercial antifreeze concentrate has up to 5 mass % electrolytes that have a severely detrimental impact on dispersion effect. For example, when replacing pure EG with Zerex Antifreeze concentrate, the otherwise stable dispersions turned into paste. The centrifuge test was used to evaluate the dispersion stability. Except for diamond, each of the other four candidates had at least one stable dispersion in EG/water (1+1) volume/volume solution (Please note, for practical purpose, the EG to D.I. water ration in this paper is always (1+1) by volume and will be simplified as EG/water). Their thermal conductivity (k) and viscosity performance at 75 °F were summarized in Table 2.

TBALE 2 (a)—*Description of five stable nano dispersion in EG/water.*

Material Supplier	Specific Description	Dispersion in EG/Water		Nano Dispersion
		mass%	volume%	
EG/Water (1+1) Volume	Base line	---	---	Base line
Alumina, Sasol Dispal X-0	113nm, powder	20	5	A
Alumina, NanoDur 1121W	45nm, 50% in water	32.3	8	B
CuO, NanoArc U1121W	30nm, 50% in water	32.3	4.8	C
SiC, Saint-Gobain	300nm, 13% in water	6	1.9	D
Graphite, Aqudag E	750nm, 22% in water	7.5	3.5	E

TBALE 2 (b)—*Thermal conductivity (k) and viscosity at 75°F of above stable nano dispersion.*

Nano Dispersion	k W/mK	k increase/%	viscosity cSt	viscosity increase/%
Base line	0.399	---	3.55	---
A	0.493	28	18.83	430
B	0.459	19	9.85	177
C	0.447	16	13.22	272
D	0.435	13	4.36	23
E	0.583	47	467	13055

Please note that sonication and adding proper dispersant are typical ways to make stable nano dispersions. Dispersants play very important role in making most effective dispersion which will be seen in this paper. The above five stable dispersions could be accomplished without using extra dispersants because the suppliers already incorporated proper dispersants into their products (concentrations or powders). In Table 2, only two nano dispersions, alumina (Sasol) and graphite (Acheson) have higher than 20% thermal conductivity increase but the viscosities increased way higher. For nano alumina dispersions, much higher particle loading were needed in order to have higher than 20% thermal conductivity increase. Based on these first stage screening experiments, nano alumina and graphite were chosen to study further.

Nano Alumina Dispersion in EG/Water

The Sasol Diapal X-0 nano alumina powder is engineered to be readily dispersed in aqueous system. It has a needle like shape. Table 3 shows summary of study of particle loading effects on thermal conductivity and viscosity. It can be seen that thermal conductivity increases lineally with the particle loading while viscosity increases exponentially. Table 4 shows the effects of using extra dispersant to reduce the viscosity increase

TABLE 3—*Alumina loading effect on k and viscosity of nano dispersion in EG/water at 75°F.*

alumina loading		k	k	viscosity	viscosity
mass %	volume %	W/mK	increase/%	cSt	increase/%
0	0	0.385	---	3.55	---
10	2.5	0.433	12	9.17	158
20	5	0.487	26	19.98	463
30	7.5	0.553	44	102.64	2790

TABLE 4—*Dispersant effect on k and viscosity of nano alumina dispersion in EG/water at 75°F.*

alumina	dispersant	k	k	viscosity	viscosity
mass %	mass %	W/mK	increase/%	cSt	increase/%
20	0.5	0.487	26	19.77	457
20	1	0.486	26	17.68	398
20	2	0.486	26	17.56	394
20	3	0.486	26	17.34	388

10	0	0.433	12	9.17	158
10	0.5	0.433	12	8.11	128
30	0	0.553	44	102.64	2790
30	1	0.549	44	72.23	1935

Note, alumina is Sasol Dispal X-0, dispersant is Solsperse 20000.

Taking both thermal conductivity and viscosity increases into account, the one with bold letters in Table 4 was chosen to do the Centrifuge Test, Boil-up Test, CID A-A-52624A Storage Stability Test, CID A-A-52624A Compatibility Test, ASTM D 1384 Corrosion Test, and ASTM D 4340 Corrosion Test. It passed the first three tests but the other three tests failed by gelling-up when it was mixed with test reference fluids. The reason for gel-up is likely due to the pH value change during dilution by the test reference fluids which exceeded the iso-electric point. The pH value of this nano alumina in water glycol solution was around 4.5 and nano alumina particles with absorbed protons repel each other, thus maintaining suspension in the dispersion. Once the pH value is higher than its iso-electric point the nano alumina dispersion just gels up.

The nano Dispersion B in Table 2 (made from NanoDur 1121W) had close to 20% increase in thermal conductivity. It is very different from Dispersion A because it passed the Centrifuge Test, CID A-A-52624A Storage Stability Test, and CID A-A-52624A Compatibility Test. However it failed the boil-up test badly: it turned into dreggy form after being cooled. This is mostly due to its high particle loading of 32.3 mass%. In addition, its viscosity reduction effort was not successful. Since its viscosity increase (177%) was almost 10 times the thermal conductivity enhancement, there was no need to run the two corrosion tests. Overall the nano alumina dispersions have a very mediocre thermal conductivity enhancement performance if viscosity increase has to be minimized. Thus further work would be focused on nano graphite dispersions.

Nano Graphite Dispersions in EG/Water

From Table 2 the most promising candidate is the nano graphite dispersion. It has a much higher thermal conductivity increase under the equivalent particle loadings. The loading and dispersant effects on nano graphite (Acheson Aquadag E) are summarized in Tables 4 and 5.

TABLE 5—*Graphite loading effect on k and viscosity of nano dispersion in EG/water at 75°F.*

graphite loading		k	k	viscosity	viscosity
mass %	volume %	W/mK	increase/%	cSt	increase/%
0	0	0.385	---	3.55	---
2.5	1.2	0.439	14	5.11	44
5	2.3	0.509	32	46.94	1222
7.5	3.5	0.583	51	467	13055
10	4.65	0.642	67	paste	

TABLE 6—*Dispersant effect on k and viscosity of nano graphite dispersion in EG/water at 75 °F.*

graphite mass %	dispersant mass %	k W/mK	k increase/%	viscosity cSt	viscosity increase/%
5	0	0.509	32	46.94	1222
5	1	0.507	32	9.3	162
5	2	0.493	28	7.08	99
5	3	0.483	25	6.67	87
5	4	0.483	25	6.34	79
2.5	0	0.439	14	5.11	44
2.5	1.5	0.421	9	4.86	37
7.5	0	0.583	51	467	13055
7.5	3	0.565	47	13.6	283
3.75	1.5	0.469	22	6.57	85
10	0	0.642	67	gel	
10	3	0.628	63	46.18	1200

Note, the graphite is Acheson Aquadag E, the dispersant is Solsperse 27000.

Here it was observed that an effective dispersant could play a very important role in reducing the viscosity. In addition, once the dispersion became more effective the thermal conductivity enhancement was compromised, which reflects the clustering mechanism in nanofluids thermal conductivity increase. The formula with bold letters in Table 6 was chosen to do the same six tests. It just passed the Centrifuge Test and the CID A-A-52624-A Storage Stability Test. However both corrosion tests failed so badly that the tests had to be aborted due to too much agglomeration. Now it was thought that if a nano dispersion didn't fare well in the boil-up test, it might not perform well during the corrosion tests. By reducing the graphite loading the formulae with bold letters in Table 7 passed the boil-up test. Then the two corrosion tests could be finished, but the results were still failure. This failure was not unusual because there were no corrosion inhibitors in the nanofluids. The next experiments would replace the EG with commercial antifreeze products.

TABLE 7—*Boil-up test result for reformulated nano graphite dispersion in EG/water.*

graphite mass %	dispersant mass %	k W/mK	k increase/%	viscosity cSt	viscosity increase/%	boil-up test
7.5	3	0.565	47	13.6	283	failed
4.4	0	0.499	30	6.55	75	failed
4.4	1	0.495	29	5.82	56	failed
4.4	2	0.490	27	6.20	67	passed

Note, the graphite is Acheson Aquadag E, the dispersant is Solsperse 27000.

Nano Graphite Dispersions in Commercial Antifreeze Zerex/Water

Three Zerex antifreeze concentrates were chosen:

Zerex G-05: Phosphate free, long life hybrid formulation, mostly used for passenger cars.

Zerex 618: Fully formulated with organic acid, mostly used for heavy duty diesel engines.

Zerex Dex-Cool: Phosphate and silicate free, organic acid technology, mostly used for GM and Asian vehicles.

Here the pure EG was replaced with Zerex antifreeze concentrates. In the finished formula Zerex to D.I. water ratio is also (1+1) by volume and will be also simplified as Zerex/water. The boil-up test results along with thermal conductivity (k) and viscosity data at 75°F are summarized in Table 8.

TABLE 8—*Boil-up test result for nano graphite dispersion in Zerex/water.*

graphite mass %	dispersant mass %	k W/mK	k increase/%	viscosity cSt	viscosity increase/%	boil-up test
Zerex G-05 based nanofluids						
0	0	0.392	---	3.96	---	---
4.4	0	gel	---	gel	---	---
4.3	2	0.513	31	13.4	238	F
4.2	4	0.503	28	10.17	157	F
4.1	6	0.485	24	9.67	144	P
Zerex 618 based nanofluids						
0	0	0.392	---	3.76	---	---
4.4	0	gel	---	gel	---	---
4.3	2	0.504	29	20.1	434	F
4.2	4	0.501	28	10.07	168	F
4.1	6	0.480	22	9.82	161	P
Zerex Dex-Cool based nanofluids						
0	0	0.389	---	3.67	---	---
4.4	0	gel	---	gel	---	---
4.3	2	0.508	31	11.56	215	F
4.2	4	0.499	28	8.24	124	P
4.1	6	0.476	22	7.17	95	P

Note, the graphite is Acheson Aquadag E, the dispersant is Solsperse 27000.

The formulae with bold letters in above Table 8 which passed boil-up tests were sent for the two corrosion tests. The results along with other test results are summarized in Table 9. The Zerex 618 based nano coolant was successful in passing both corrosion tests. But it failed the CID A-A-62624-A storage stability and compatibility tests. The next effort was to find a more effective dispersant.

TABLE 9—*Test results for nano graphite dispersion in EG/water and Zerex/water.*

medium base	graphite mass %	dispersant mass %	boil-up test	centrifuge Out/%	storage stability	compatibility test	D 1384 test	D 4340 test
EG	4.4	2	P	1.3	P	F	F ^a	F
G-05	4.1	6	P	12.7	F	F	F ^b	P
618	4.1	6	P	15.8	F	F	P	P
Dex-Cool	4.2	4	P	14.9	F	F	F ^c	P

Note, the graphite is Acheson Aquadag E, the dispersant is Solsperse 27000.

^a failed in Iron, Steel, Brass and Solder, passed on Aluminum and Copper.

^b failed in Iron only.

^c failed in Iron only.

Nano Graphite Dispersions with New Dispersant in Commercial Antifreeze Zerex/Water

After the new dispersant, Dispersant T (trade secret), had been identified, not only Zerex 618 based formula passed all the tests, the Zerex G-05 based formula also passed all tests. While the Zerex Dex-Cool based formula only failed the Aluminum in the ASTM D 1384 corrosion test (see Table 10 and 11). The pictures of end-of –test (EOT) coupon assembly can be reviewed in Fig. 2 where the Zerex 618 based nano coolant had hardly left any deposit on the coupons. Fig. 3 shows images of EOT specimens of ASTM D 4340 corrosion test where bigger particles had settled down over time. All EOT coupons and specimens were washable with water though. Based on the observation of EOT coupon assembly, Zerex 618 was preferred to Zerex G-05.

TABLE 10—*Boil-up test result for nano graphite dispersion with Dispersant T in Zerex/water.*

medium base	graphite mass %	dispersant mass %	k W/mK	k increase/%	viscosity cSt	viscosity increase/%	boil-up test
G-05	4.2	5	0.488	25	6.89	74	P
618	4.2	5	0.489	25	6.91	84	P
Dex-Cool	4.2	4	0.488	25	6.20	69	P

Note, the graphite is Acheson Aquadag E, the dispersant is Dispersant T (trade secret).

TABLE 11—*Test results for nano graphite dispersion with Dispersant T in Zerex/water.*

medium base	graphite mass %	dispersant mass %	boil-up test	centrifuge Out/%	storage stability	compatibility test	D 1384 test	D 4340 test
G-05	4.2	5	P	13.8	P	P	P	P
618	4.2	5	P	14.2	P	P	P	P
Dex-Cool	4.2	4	P	14.1	P	P	F ^a	P

Note, the graphite is Acheson Aquadag E, the dispersant is Dispersant T (trade secret).

^a failed in Aluminum only.

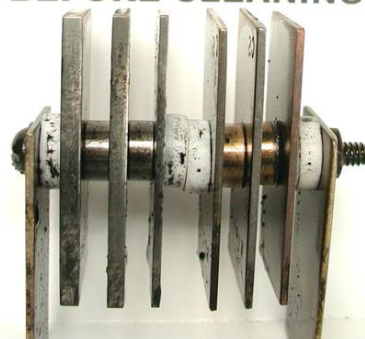
ASTM CORROSION TEST**C7455-177-1****BEFORE CLEANING****ASTM CORROSION TEST****C7455-177-2****BEFORE CLEANING**

FIG. 2—The end-of-test coupon assembly of corrosion test D 1384 for nano graphite (Acheson Aquadag E) in Zerex G-05/water (left) and Zerex 618/water (right).

ASTM CORROSION TEST**C7455-177-1****BEFORE CLEANING****ASTM CORROSION TEST****C7455-177-2****BEFORE CLEANING**

FIG. 3—The end-of-test specimen of corrosion test D 4340 for nano graphite (Acheson Aquadag E) in Zerex G-05/water (left) and Zerex 618/water (right).

Conclusions

Although nano alumina dispersions have been the most popular research subject in the nanofluid domain [11], this paper has demonstrated that properly engineered nano graphite dispersions can be of much more practical application. This is especially true taking divergent performance attributes into account: significant thermal conductivity increases, minimal viscosity increase, low density for better dispersion stability, and relatively low cost, among others. An in-house centrifuge test was used to evaluate the nano dispersion stability and a boil-up test was explored to serve as a screening test to see whether a nano dispersion would survive high temperatures in engine coolant corrosion tests. Without corrosion inhibitors, the nano coolants failed the corrosion tests. Without an effective dispersant, the nano graphite coolant could not pass the CID

AA-52624A compatibility and storage stability tests. After making adjustments in particle loading, identifying an effective dispersant, and establishing proper dispersant levels, one commercial nano graphite concentrate was successfully integrated into commercial antifreeze Zerex 618. It passed both engine coolant corrosion tests ASTM D 1384 and ASTM D 4340 plus the CID AA-52624A compatibility and storage stability tests. Compared with the base coolant, the nano graphite coolant has more than a 25% increase in thermal conductivity at 2 volume percent particle loading, which is an anomalous enhancement.

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